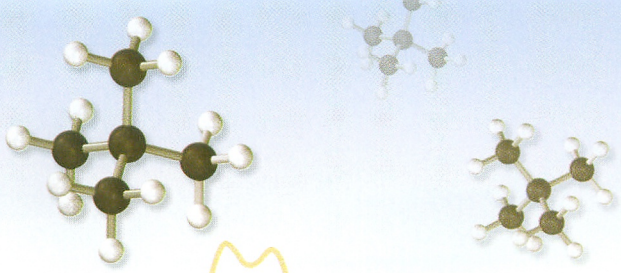
VISIT…



Brief Contents

1 A Simple Model for Chemical Bonds **1**

2 Organic Compounds: A First Look **30**

3 Orbitals and Bonding **61**

4 The Acid–Base Reaction **103**

5 Functional Groups and Nomenclature I **142**

6 Stereochemistry I: Cis–Trans Isomers and Conformations **178**

7 Stereochemistry II: Chiral Molecules **219**

8 Nucleophilic Substitution Reactions: Reactions of Alkyl Halides, Alcohols, and Related Compounds **257**

9 Elimination Reactions: Reactions of Alkyl Halides, Alcohols, and Related Compounds **313**

10 Synthetic Uses of Substitution and Elimination Reactions: Interconverting Functional Groups **348**

11 Additions to Carbon–Carbon Double and Triple Bonds: Reactions of Alkenes and Alkynes **404**

12 Functional Groups and Nomenclature II **466**

13 Infrared Spectroscopy **500**

14 Nuclear Magnetic Resonance Spectroscopy **543**

15 Ultraviolet-Visible Spectroscopy and Mass Spectrometry **609**

16 Benzene and Aromatic Compounds **642**

17 Aromatic Substitution Reactions **671**

18 Additions to the Carbonyl Group: Reactions of Aldehydes and Ketones **739**

19 Substitutions at the Carbonyl Group: Reactions of Carboxylic Acids and Derivatives **803**

20 Enolate and Other Carbon Nucleophiles **858**

21 The Chemistry of Radicals **918**

22 Pericyclic Reactions **956**

23 The Synthesis of Organic Compounds **1011**

24 Synthetic Polymers **1053**

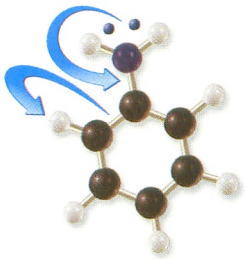
25 Carbohydrates **1085**

26 Amino Acids, Peptides, and Proteins **1123**

27 Nucleotides and Nucleic Acids **1162**

28 Other Natural Products **1184**

Contents



PREFACE xxvi

1 A SIMPLE MODEL FOR CHEMICAL BONDS 1

1.1 The Field of Organic Chemistry 1
1.2 Simple Atomic Structure 3
1.3 Ionic Bonding 4
1.4 Covalent Bonding 5
1.5 Lewis Structures 6
1.6 Covalent Ions 11
1.7 Formal Charges 11
1.8 Resonance 15
1.9 Polar Bonds 17
1.10 Shapes of Molecules 18
1.11 Dipole Moments 22
Review of Mastery Goals 24
Additional Problems 25

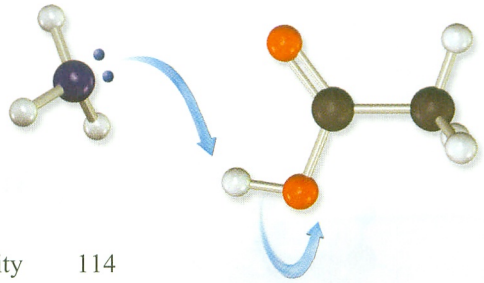
2 ORGANIC COMPOUNDS: A FIRST LOOK 30

2.1 Common Bonding Situations 30
2.2 Bond Strengths and Bond Lengths 33
2.3 Constitutional Isomers 34
2.4 Degree of Unsaturation 39
2.5 Physical Properties and Molecular Structure 44
2.6 Melting Points, Boiling Points, and Solubilities 46
Focus On: Boiling Points of Fuels 48
2.7 Introduction to Functional Groups 50
Review of Mastery Goals 52
Additional Problems 53

3 ORBITALS AND BONDING 61

3.1 Atomic Orbitals 61
3.2 Molecular Orbitals 65
3.3 Single Bonds and sp^3 Hybridization 69
3.4 Double Bonds and sp^2 Hybridization 71
3.5 Triple Bonds and sp Hybridization 76

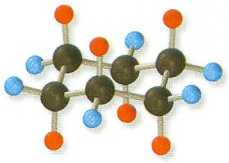
3.6 Resonance and MO Theory 78
3.7 Rules for Resonance Structures 81
3.8 Types of Resonance Interactions 86
Focus On: Resonance and the Bond Lengths of Naphthalene 94
3.9 Molecular Orbital Energies 95
Review of Mastery Goals 97
Additional Problems 97



4 The Acid–Base Reaction 103
4.1 Definitions 103
4.2 The Acid–Base Equilibrium 107
4.3 Rate of the Acid–Base Reaction 111
4.4 Effect of the Atom Bonded to the Hydrogen on Acidity 114
4.5 Inductive Effects 116
4.6 Hydrogen Bonding 119
4.7 Hybridization 120
4.8 Resonance 120
Focus On: Calcium Carbide 121
4.9 Tables of Acids and Bases 128
4.10 Acidity and Basicity of Functional Groups and Solvents 132
Review of Mastery Goals 135
Additional Problems 135

5 Functional Groups and Nomenclature I 142
5.1 Alkanes 142
5.2 Common Nomenclature of Alkanes 145
5.3 Systematic Nomenclature of Alkanes 146
Focus On: The Energy Content of Fuels 146
5.4 Systematic Nomenclature of Cycloalkanes 155
5.5 Alkenes 157
5.6 Alkynes 160
5.7 Alkyl Halides 161
5.8 Alcohols 162
Focus On Biological Chemistry: Chlorinated Organic Compounds 164
5.9 Ethers 167
5.10 Amines 168
Review of Mastery Goals 171
Additional Problems 172

6 Stereochemistry I: Cis–Trans Isomers and Conformations 178
6.1 Cis–Trans Isomers 179
6.2 Designating the Configuration of Cis–Trans Isomers 183
6.3 Conformations 186



6.4 Conformations of Cyclic Molecules 193
6.5 Conformations of Cyclohexane 196
6.6 Conformations of Other Rings 201
6.7 Conformations of Cyclohexanes with One Substituent 202
6.8 Conformations of Cyclohexanes with Two or More Substituents 205
Focus On: How Much Strain Is Too Much? 206
Review of Mastery Goals 214
Additional Problems 214

7 STEREOCHEMISTRY II: CHIRAL MOLECULES 219

7.1 Chiral Molecules 219
7.2 Recognizing Chiral Molecules 221
7.3 Designating Configuration of Enantiomers 224
7.4 Properties of Enantiomers 227
7.5 Molecules with Multiple Chirality Centers 230
7.6 Stereoisomers and Cyclic Compounds 234
7.7 Resolution: Separating Enantiomers 236
7.8 Fischer Projections 237
Focus On: The Historical Development of Understanding Stereochemistry 238
7.9 Reactions That Produce Enantiomers 242
Focus On: Pharmaceuticals and Chirality 243
7.10 Other Chiral Compounds 244
Review of Mastery Goals 247
Visual Summary of Isomers 248
Additional Problems 249

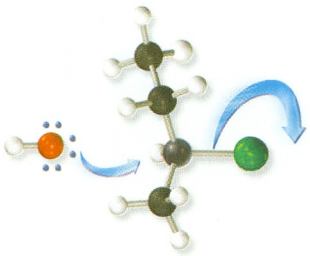
8 NUCLEOPHILIC SUBSTITUTION REACTIONS: REACTIONS OF ALKYL HALIDES, ALCOHOLS, AND RELATED COMPOUNDS 257

8.1 The General Reaction 257
8.2 Reaction Mechanisms 259
8.3 Bimolecular Nucleophilic Substitution 259
8.4 Stereochemistry of the S_N2 Reaction 261
8.5 Effect of Substituents on the Rate of the S_N2 Reaction 264
8.6 Unimolecular Nucleophilic Substitution 268
8.7 Effect of Substituents on the Rate of the S_N1 Reaction 272
Focus On: The Triphenylmethyl Carbocation 274
8.8 Stereochemistry of the S_N1 Reaction 276
8.9 Leaving Groups 279
8.10 Nucleophiles 284
8.11 Effect of Solvent 286
8.12 Competition between S_N1 and S_N2 Reactions 289
8.13 Intramolecular Reactions 292
8.14 Competing Reactions 294

Focus On: Carbocation Rearrangements in Superacids 299
Review of Mastery Goals 301
Visual Summary of Key Reactions 301
Additional Problems 302

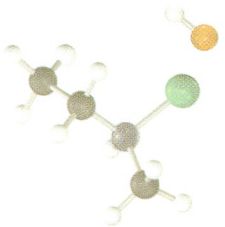
9 ELIMINATION REACTIONS: REACTIONS OF ALKYL HALIDES, ALCOHOLS, AND RELATED COMPOUNDS 313

9.1 The General Reaction 313
9.2 Bimolecular Elimination 314
Focus On Biological Chemistry: DDT-Resistant Insects 316
9.3 Stereochemistry of the E2 Reaction 316
9.4 Direction of Elimination 323
9.5 Unimolecular Elimination 329
9.6 Regiochemistry and Stereochemistry of the E1 Reaction 331
Focus On: The E1cb Mechanism 333
9.7 The Competition between Elimination and Substitution 334
Focus On Biological Chemistry: Biological Elimination Reactions 340
Review of Mastery Goals 341
Visual Summary of Key Reactions 341
Additional Problems 341

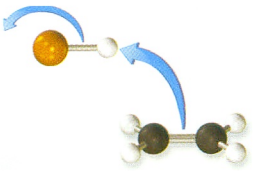


10 SYNTHETIC USES OF SUBSTITUTION AND ELIMINATION REACTIONS: INTERCONVERTING FUNCTIONAL GROUPS 348

10.1 Substitution Reactions 348
10.2 Preparation of Alcohols 349
10.3 Preparation of Ethers 352
10.4 Preparation of Esters 357
10.5 Preparation of Alkyl Halides 358
10.6 Preparation of Amines 362
Focus On Biological Chemistry: Biological Alkylations and Poisons 365
10.7 Preparation of Hydrocarbons 368
10.8 Formation of Carbon–Carbon Bonds 369
10.9 Phosphorus and Sulfur Nucleophiles 371
10.10 Ring Opening of Epoxides 372
Focus On: Uses of Epoxides in Industry 375
10.11 Elimination of Hydrogen Halides (Dehydrohalogenation) 376
10.12 Preparation of Alkynes 377
10.13 Dehydration 378
10.14 Eliminations to Form Carbon–Oxygen Double Bonds; Oxidation Reactions 380
Focus On: Environmentally Friendly Chemistry (Green Chemistry) 384
10.15 The Strategy of Organic Synthesis 385



Review of Mastery Goals 389
Visual Summary of Key Reactions 390
Integrated Practice Problem 394
Additional Problems 395



11 ADDITIONS TO CARBON–CARBON DOUBLE AND TRIPLE BONDS: REACTIONS OF ALKENES AND ALKYNES 404

11.1 The General Mechanism 405
11.2 Addition of Hydrogen Halides 406
11.3 Addition of Water (Hydration) 412
11.4 Addition of Halogens 413
11.5 Halohydrin Formation 419
Focus On: Industrial Addition Reactions 421
11.6 Oxymercuration–Reduction 423
11.7 Hydroboration–Oxidation 426
Focus On: Chiral Boranes in Organic Synthesis 433
11.8 Addition of Carbenes 435
11.9 Epoxidation 438
11.10 Hydroxylation 439
11.11 Ozonolysis 441
11.12 Catalytic Hydrogenation 444
11.13 Additions to Conjugated Dienes 446
Focus On: Asymmetric Hydrogenation 449
11.14 Synthesis 451
Review of Mastery Goals 453
Visual Summary of Key Reactions 454
Integrated Practice Problem 457
Additional Problems 458

12 FUNCTIONAL GROUPS AND NOMENCLATURE II 466

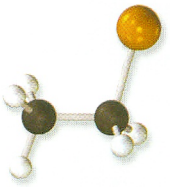
12.1 Aromatic Hydrocarbons 466
Focus On: Structure Proof by the Number of Isomers 469
12.2 Phenols 472
12.3 Aldehydes and Ketones 473
12.4 Carboxylic Acids 477
12.5 Derivatives of Carboxylic Acids 479
Focus On: Fragrant Organic Compounds 486
12.6 Sulfur and Phosphorus Compounds 488
12.7 Nomenclature of Compounds with Several Functional Groups 491
Review of Mastery Goals 494
Additional Problems 494

13 INFRARED SPECTROSCOPY 500

13.1 Electromagnetic Radiation 501
13.2 Interaction of Electromagnetic Radiation with Molecules 502
13.3 The Electromagnetic Spectrum 503
13.4 Infrared Spectroscopy 505
13.5 Generalizations 507
13.6 The Hydrogen Region 508
13.7 The Triple-Bond Region 515
Focus On: Remote Sensing of Automobile Pollutants 516
13.8 The Double-Bond Region 518
13.9 The Fingerprint Region 520
13.10 Interpretation of IR Spectra 521
Review of Mastery Goals 533
Additional Problems 533

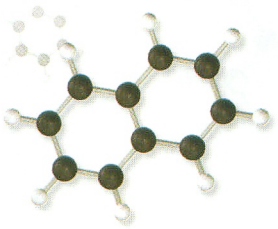
14 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY 543

14.1 Proton Magnetic Resonance Spectroscopy 543
14.2 Theory of ^{1}H-NMR 545
14.3 The Chemical Shift 547
14.4 Spin Coupling 556
14.5 Complex Coupling 562
14.6 Chemical Exchange 563
14.7 Deuterium 563
Focus On: NMR Spectroscopy of Carbocations in Superacid 565
14.8 Interpretation of ^{1}H-NMR Spectra 566
Focus On: Magnetic Resonance Imaging 572
14.9 Carbon-13 Magnetic Resonance Spectroscopy 574
14.10 Solved Problems Employing IR and NMR Spectra 583
Review of Mastery Goals 595
Additional Problems 596



15 ULTRAVIOLET-VISIBLE SPECTROSCOPY AND MASS SPECTROMETRY 609

15.1 Ultraviolet-Visible Spectroscopy 609
15.2 Types of Electronic Transitions 612
15.3 UV-Visible Spectroscopy in Structure Determination 615
Focus On: Ozone, Ultraviolet Radiation, and Sunscreens 616
15.4 Mass Spectrometry 617
15.5 Determining the Molecular Formula 619
15.6 Fragmentation of the Molecular Ion 624
Focus On: Gas Chromatography and Mass Spectrometry 633
Review of Mastery Goals 634
Additional Problems 634



16 Benzene and Aromatic Compounds 642

16.1 Benzene 642
16.2 Resonance Energy of Benzene 644
16.3 Molecular Orbital Model for Cyclic Conjugated Molecules 646
16.4 Cyclobutadiene 649
16.5 Hückel's Rule 651
16.6 Cyclooctatetraene 652
16.7 Heterocyclic Aromatic Compounds 653
16.8 Polycyclic Aromatic Hydrocarbons 655
Focus On: Carcinogenic Polycyclic Aromatic Hydrocarbons 657
16.9 NMR and Aromaticity 657
16.10 Annulenes 659
16.11 Aromatic and Antiaromatic Ions 661
Focus On: Buckminsterfullerene, a New Form of Carbon 663
Review of Mastery Goals 665
Additional Problems 665

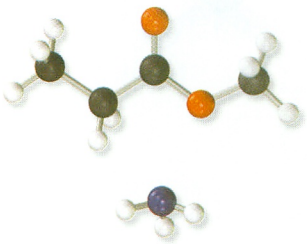
17 Aromatic Substitution Reactions 671

17.1 Mechanism for Electrophilic Aromatic Substitution 671
17.2 Effect of Substituents 674
17.3 Effect of Multiple Substituents 682
17.4 Nitration 683
17.5 Halogenation 686
17.6 Sulfonation 689
17.7 Friedel-Crafts Alkylation 690
Focus On: Synthetic Detergents, BHT, and BHA 694
17.8 Friedel-Crafts Acylation 696
17.9 Electrophilic Substitutions of Polycyclic Aromatic Compounds 699
17.10 Nucleophilic Aromatic Substitution: Diazonium Ions 700
17.11 Nucleophilic Aromatic Substitution: Addition–Elimination 703
17.12 Nucleophilic Aromatic Substitution: Elimination–Addition 705
Focus On: Experimental Evidence for the Benzyne Mechanism 708
17.13 Some Additional Useful Reactions 709
17.14 Synthesis of Aromatic Compounds 713
Review of Mastery Goals 719
Visual Summary of Key Reactions 719
Integrated Practice Problem 723
Additional Problems 724

18 Additions to the Carbonyl Group: Reactions of Aldehydes and Ketones 739

18.1 General Mechanisms 740
18.2 Addition of Hydride; Reduction of Aldehydes and Ketones 742

18.3 Addition of Water 744
18.4 Addition of Hydrogen Cyanide 748
18.5 Preparation and Properties of Organometallic Nucleophiles 751
18.6 Addition of Organometallic Nucleophiles 753
18.7 Addition of Phosphorus Ylides; The Wittig Reaction 758
Focus On: Synthesis of Vitamin A 763
18.8 Addition of Nitrogen Nucleophiles 765
Focus On Biological Chemistry: Imines in Living Organisms 773
18.9 Addition of Alcohols 775
18.10 Conjugate Additions 779
18.11 Synthesis 784
Review of Mastery Goals 787
Visual Summary of Key Reactions 787
Integrated Practice Problem 789
Additional Problems 790

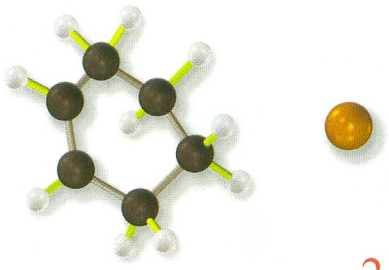


19 Substitutions at the Carbonyl Group: Reactions of Carboxylic Acids and Derivatives 803

19.1 The General Mechanism 803
19.2 Preparation of Acyl Chlorides 808
19.3 Preparation of Anhydrides 810
19.4 Preparation of Esters 811
19.5 Preparation of Carboxylic Acids 815
Focus On: The Preparation of Soap 819
19.6 Preparation of Amides 824
19.7 Reaction with Hydride Nucleophiles 826
19.8 Reduction of Acid Derivatives to Aldehydes 830
19.9 Reactions with Organometallic Nucleophiles 832
19.10 Preparation of Ketones 834
19.11 Derivatives of Sulfur and Phosphorus Acids 836
Focus On Biological Chemistry: Nerve Gases and Pesticides 838
Review of Mastery Goals 840
Visual Summary of Key Reactions 840
Integrated Practice Problem 843
Additional Problems 843

20 Enolate and Other Carbon Nucleophiles 858

20.1 Enols and Enolate Anions 859
20.2 Halogenation of the α-Carbon 862
20.3 Alkylation of Enolate Anions 864
20.4 Alkylation of More Stabilized Anions 867
20.5 The Aldol Condensation 873
Focus On Biological Chemistry: The Reverse Aldol Reaction in Metabolism 880
20.6 Ester Condensations 880



Focus On: An Industrial Aldol Reaction 886
20.7 Carbon and Hydrogen Leaving Groups 887
20.8 Enamines 889
20.9 Other Carbon Nucleophiles 891
20.10 Conjugate Additions 894
20.11 Synthesis 898
Review of Mastery Goals 902
Visual Summary of Key Reactions 902
Integrated Practice Problem 904
Additional Problems 905

21 THE CHEMISTRY OF RADICALS 918
21.1 Radicals 918
21.2 Stability of Radicals 919
21.3 Geometry of Carbon Radicals 921
21.4 Generation of Radicals 922
21.5 General Radical Reactions 923
Focus On: The Triphenylmethyl Radical 926
21.6 Halogenation 927
21.7 Dehalogenation 934
21.8 Autoxidation 935
Focus On Biological Chemistry: Vitamin E and Lipid Autoxidation 937
21.9 Radical Additions to Alkenes 939
21.10 Reductions and Radical Anions 941
Review of Mastery Goals 946
Visual Summary of Key Reactions 947
Additional Problems 948

22 PERICYCLIC REACTIONS 956
22.1 Pericyclic Reactions 956
22.2 MO Theory for Conjugated Molecules 959
22.3 Electrocyclic Reactions 965
22.4 Examples of Electrocyclic Reactions 970
Focus On: Dewar Benzene 973
22.5 Cycloaddition Reactions 975
22.6 The Diels-Alder Reaction 977
22.7 Other Cycloaddition Reactions 984
22.8 Sigmatropic Rearrangements 986
22.9 Examples of Sigmatropic Rearrangements 990
Focus On Biological Chemistry: Pericyclic Reactions and Vitamin D 993
22.10 Rearrangements to Electron-Deficient Centers 994
Review of Mastery Goals 999
Visual Summary of Key Reactions 999
Additional Problems 1001

23 The Synthesis of Organic Compounds 1011

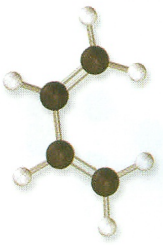
23.1 Protecting Groups for Alcohols 1011
23.2 Protecting Groups for Aldehydes and Ketones 1015
23.3 Protecting Groups for Carboxylic Acids 1016
23.4 Protecting Groups for Amines 1018
23.5 Retrosynthetic Analysis 1020
Focus On Biological Chemistry: Pheromones 1025
23.6 Examples of Syntheses 1026
23.7 Reactions That Form Carbon–Carbon Bonds 1029
23.8 Preparation of Functional Groups 1030
Review of Mastery Goals 1045
Additional Problems 1046

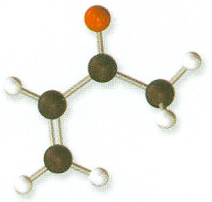
24 Synthetic Polymers 1053

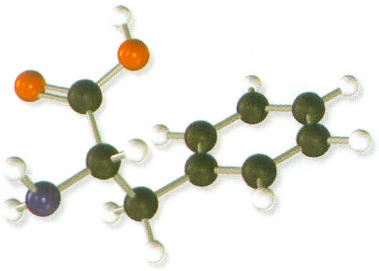
24.1 Radical Chain Polymerization 1053
24.2 Structures of Polymers 1057
24.3 Ionic Polymerization 1060
Focus On: Super Glue 1062
24.4 Coordination Polymerization 1062
24.5 Physical Properties of Polymers 1064
24.6 Major Thermoplastic Addition Polymers 1066
24.7 Elastomers 1068
24.8 Condensation Polymers 1070
24.9 Thermoset Polymers 1075
24.10 Chemical Properties of Polymers 1077
Focus On: Recycling Plastics 1080
Review of Mastery Goals 1081
Additional Problems 1081

25 Carbohydrates 1085

25.1 Structures of Carbohydrates 1085
25.2 Stereochemistry of Carbohydrates 1086
25.3 Cyclization of Monosaccharides 1090
25.4 Reactions of Monosaccharides 1094
Focus On: The Determination of Anomer Configuration 1095
Focus On: Artificial Sweeteners 1103
25.5 Fischer's Structure Proof for Glucose 1105
25.6 Disaccharides 1110
25.7 Polysaccharides 1111
25.8 Other Carbohydrate-Containing Compounds 1113
Focus On Biological Chemistry: Blood Groups 1115
Review of Mastery Goals 1116
Additional Problems 1117

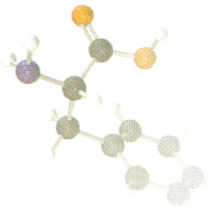






26 AMINO ACIDS, PEPTIDES, AND PROTEINS 1123

26.1 Amino Acids 1123
26.2 Acid–Base Chemistry of Amino Acids 1126
26.3 Chemical Reactions of Amino Acids 1130
26.4 Laboratory Synthesis of Amino Acids 1131
Focus On: Asymmetric Synthesis of Amino Acids 1135
26.5 Peptides and Proteins 1137
Focus On: NMR Spectra of Amides 1140
26.6 Sequencing Peptides 1140
26.7 Laboratory Synthesis of Peptides 1148
26.8 Protein Structure 1155
26.9 Enzymes 1156
Review of Mastery Goals 1158
Additional Problems 1158



27 NUCLEOTIDES AND NUCLEIC ACIDS 1162

27.1 Nucleosides and Nucleotides 1162
27.2 Structure of DNA and RNA 1165
Focus On: Tautomers of Guanine and Thymine 1170
27.3 Replication, Transcription, and Translation 1171
Focus On Biological Chemistry: Treatment of AIDS with AZT 1174
27.4 Sequencing DNA 1175
27.5 Laboratory Synthesis of DNA 1178
Review of Mastery Goals 1180
Additional Problems 1181

28 OTHER NATURAL PRODUCTS 1184

28.1 Terpenes 1184
28.2 Monoterpenes 1186
28.3 Sesquiterpenes 1190
28.4 Larger Terpenes 1194
28.5 Steroids 1196
Focus On: Syntheses That Mimic Nature 1200
28.6 Synthesis of Steroids 1202
Focus On: The Birth Control Pill 1204
28.7 Alkaloids 1206
28.8 Fats and Related Compounds 1208
Focus On: Partially Hydrogenated Vegetable Oil 1210
28.9 Prostaglandins 1211
Review of Mastery Goals 1213
Additional Problems 1213

APPENDIX: ANSWERS TO IN-CHAPTER PROBLEMS A-0

GLOSSARY G-0

INDEX I-0